Chemical Warfare Agent Simulants Project

Mr. Frank Palya, NIOSH

Principal Investigator: Dr. Donald Rivin of SBCCOM

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Project Overview

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Background

- NIOSH Public Meeting held in April 2001, some respirator manufacturers requested that NIOSH identify simulants for CBRN respirator standards.
- International Safety Equipment Association (ISEA) letter to NIOSH, January 22, 2002 requested NIOSH develop surrogate test agents.
- Although significant number of studies on the permeation effects of CWA simulants through barrier materials, inadequate data available to derive a reliable correlation between the simulants and CWA.
- Two categories of Simulants being addressed: 1) Adsorption for filtration on activated carbon. 2) Permeation through barrier materials.
- The correlation coefficient of a simulant to a CWA may be different for different barrier material (Correlation Coefficient Material Dependent).

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Project Purpose / Objective

- Category 1; Adsorption Simulants:
- **Purpose:**

  Identify a chemical compound(s) that simulates the adsorption of Sarin (GB) nerve agent and Sulfur Mustard (HD) blister agent on activated carbon.

- **Objective:**

  To identify through research chemical compound(s) that can be used as adsorption simulants for filtration effects on activated carbon and to identify pertinent reports that are available to the public.

Project Purpose / Objective (continue)

- Category 2; Purpose of Simulant Permeation Study:

  Through research and testing, identify chemical compounds to simulate the penetration and permeation effects of GB and HD through barrier materials.

- Objective:

  Identify simulants and laboratory procedures that can be used by manufacturers for estimating GB and HD blister agent permeation through barrier materials used to manufacture respirators.

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Goal: Low cost, rapid, simulant screening method for determining agent barrier performance.

Approach:

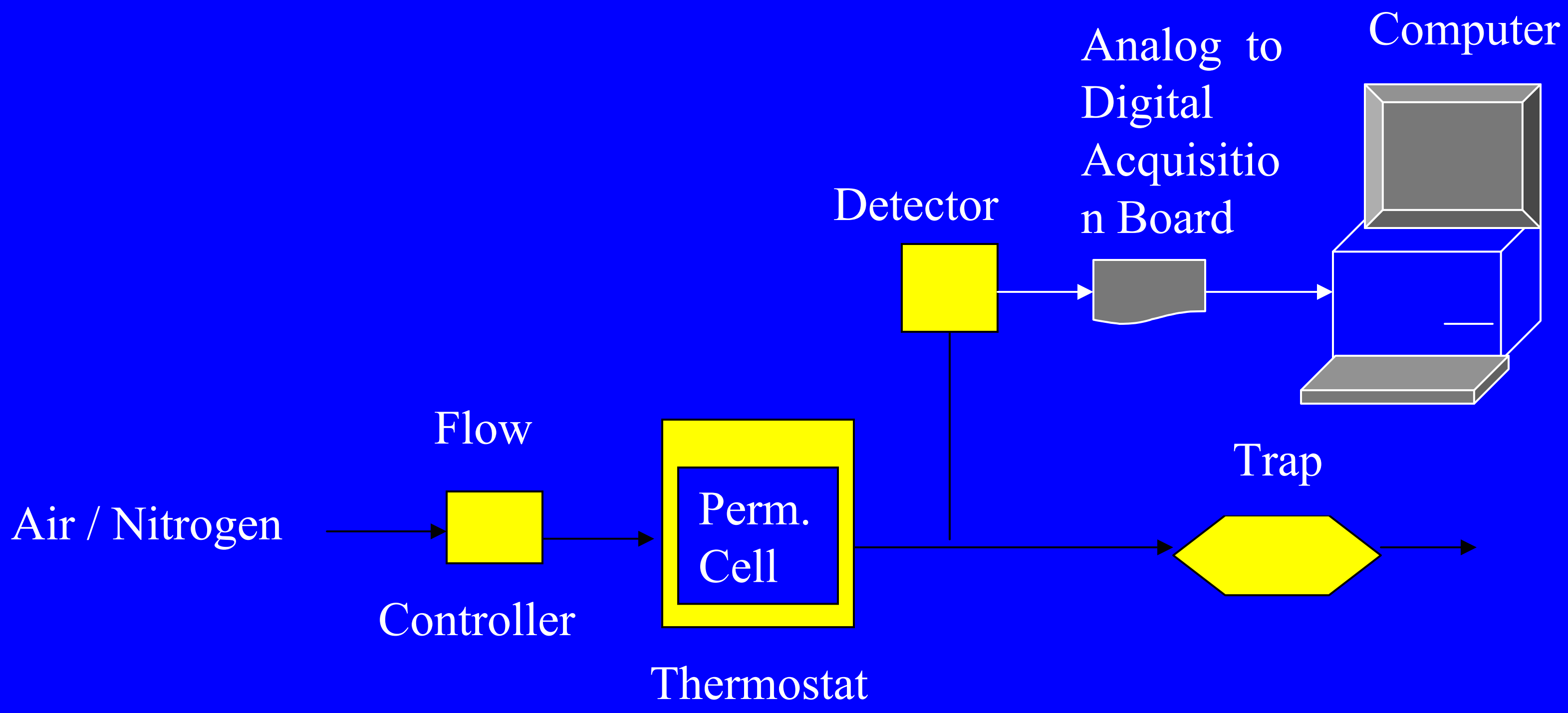
1) Develop an inexpensive permeation system with a new cell design for testing both hard and soft materials up to at least 1 cm thick.

2) Select relatively nontoxic simulants for HD and GB based on solubility in standard polymers.

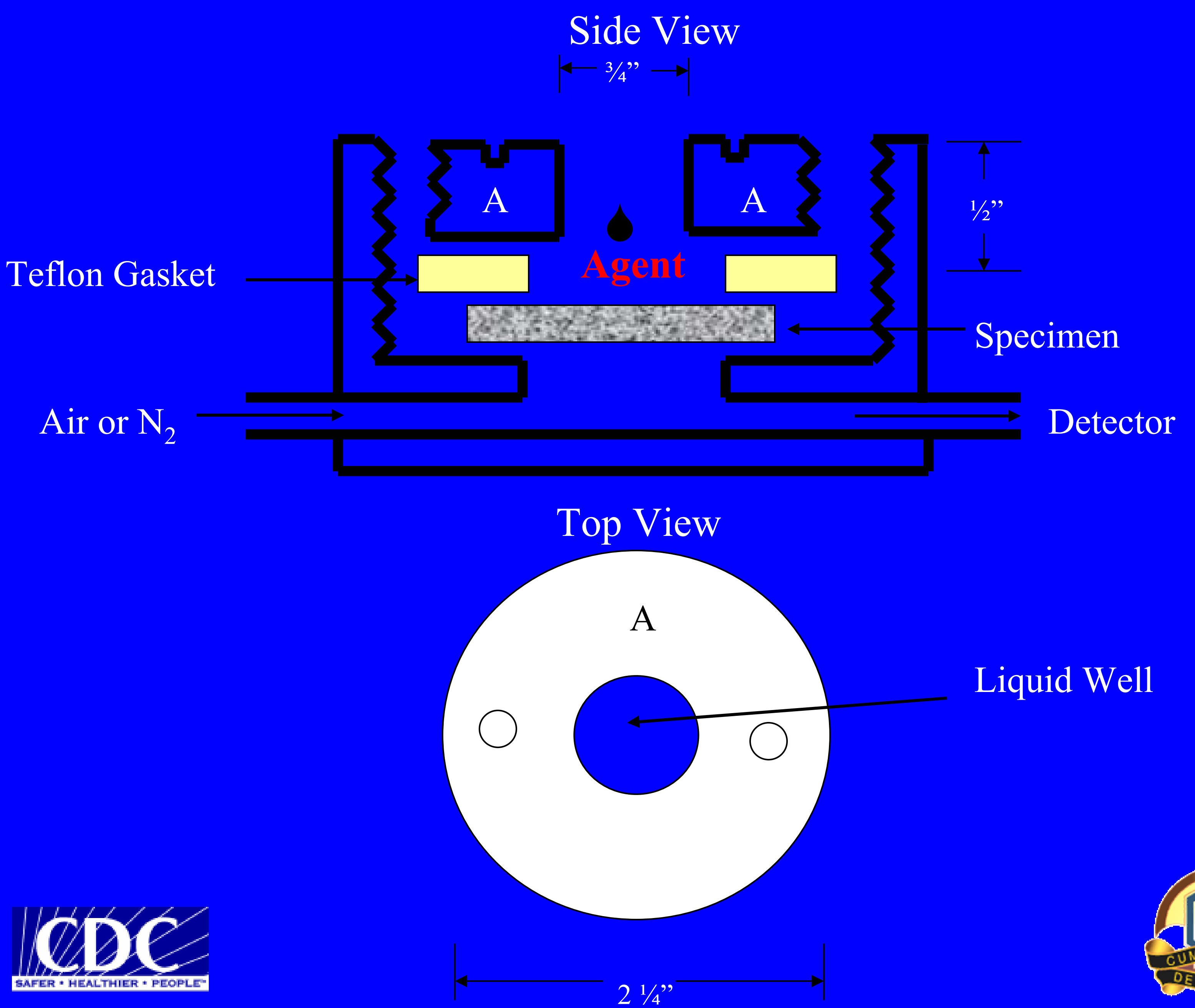
3) Employ permeation of agents and selected simulants to develop criteria for predicting resistance to agent penetration.

Technical Details

Permeation Test System



Liquid Permeation Cell



The Selection of Elastomeric Barrier Materials

Preliminary permeation and immersion testing was conducted on specimens of seven reinforced, cured elastomer compounds known to span a wide range in barrier properties. From this group, three were selected as standard materials for comparative testing with agents (HD, GB) and simulants. The test materials with specimen thickness selected to obtain convenient breakthrough time are:

Butyl Rubber (IIR): 11 - 15 mil

Ethylene-Propylene-Diene-Monomer (EPDM): 18 – 30 mil

Silicone Rubber (PDMS): 123 – 128 mil

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Permeability (P) of Organic Molecules in Polymers via Solution - Diffusion

$$P = D \bullet S \bullet L^{-1}$$

For each polymer at a specified temperature:

Diffusion Coefficient (D) = f(molecular size, concentration)

Equilibrium Solubility (S) = f(chemical interaction, concentration)

Specimen Thickness = L

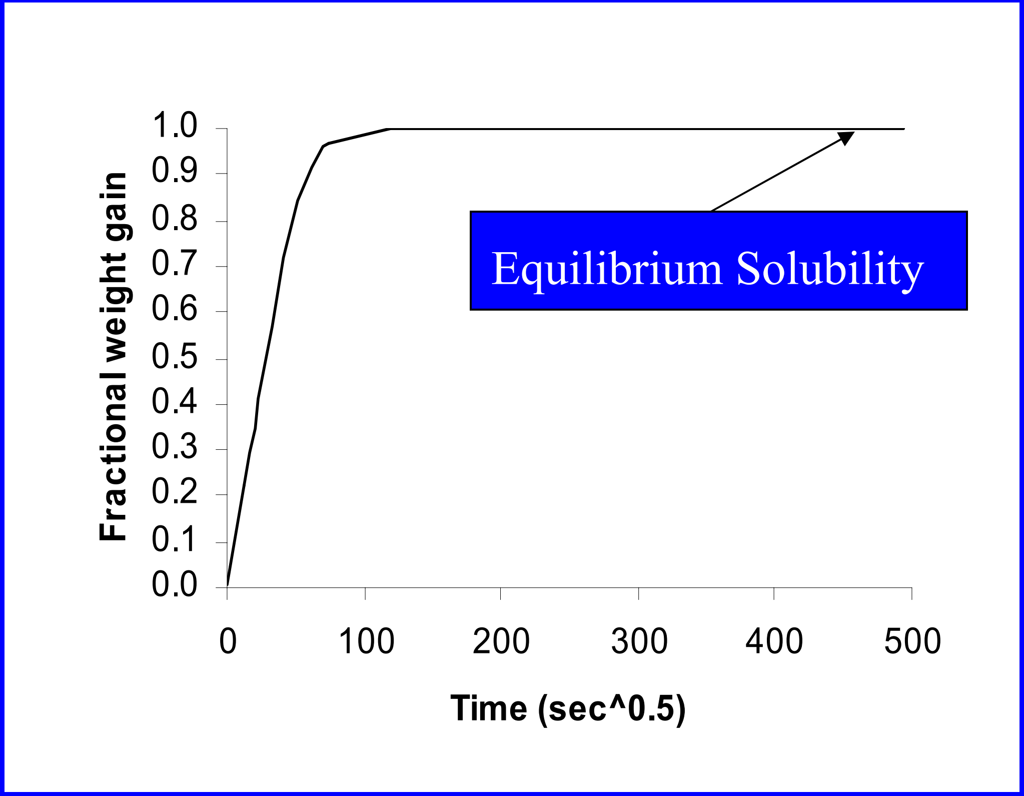
Simulants which have a solubility similar to that of agents in the materials of interest will provide the most reliable prediction of agent permeation.

Diffusion Coefficient (D) and Solubility (S) by Immersion:

Fickian Model $\delta c/\delta t = D^{\bullet}\, \delta^2 c/\delta x^2$

$S = C_{\lim t \to \infty}$

Theoretical Curve



Liquid Simulant Candidates

HD Simulants

DCH* - 1,6-Dichlorohexane

DBSS – Di-n-butyl disulfide

BCBE – Bis 4-chlorobutyl ether

CEPS* - 2-Chloroethyl phenyl sulfide

CECS - 2-Chloroethyl cyclohexyl sulfide

DBS - Dibutyl sulfide

GB Simulants

DMMP – Dimethyl methylphosphonate

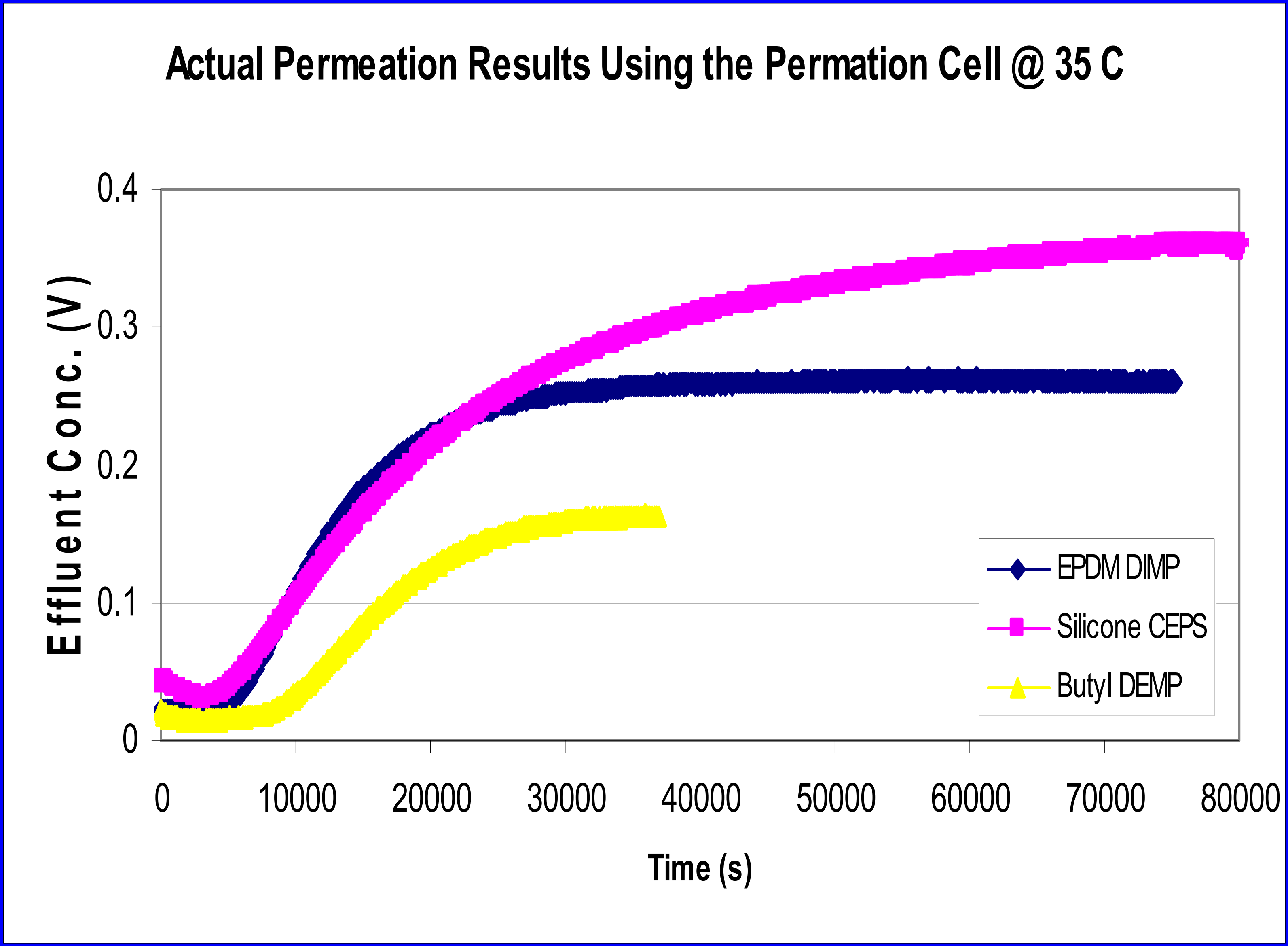
DEMP* – Diethyl methanephosphonate

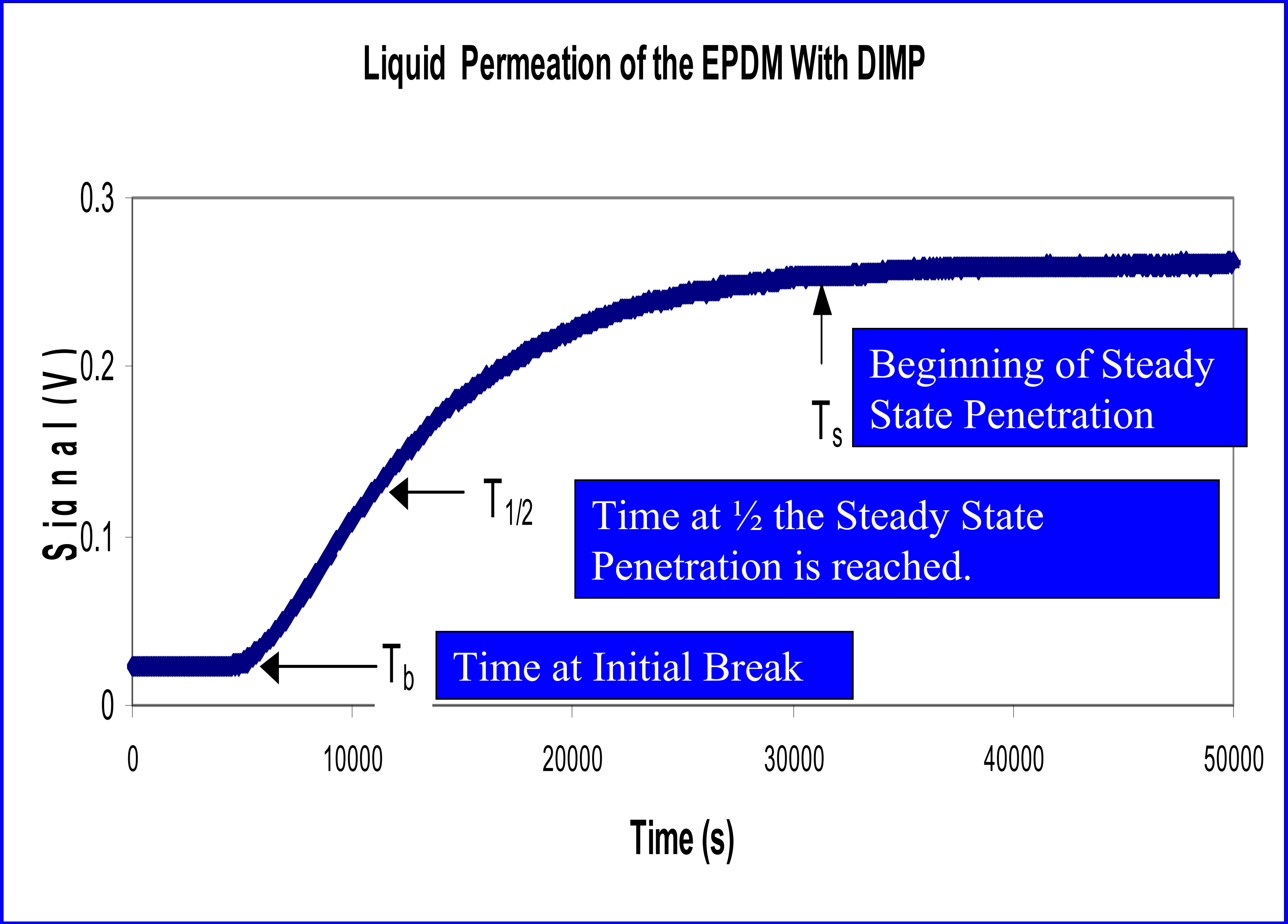
DEEP – Diethyl ethanephosphonate

DIMP* - Diisopropyl methylphosphonate

TEP – Triethyl phosphate

* prime candidates


Actual Permeation Results Using the Permation Cell @ 35 C
Effluent Conc. (V)
0.4
0.3
0.2
0.1
0
0
10000
20000
30000
40000
50000
60000
70000
80000
Time (s)
EPDM DIMP
Silicone CEPS
Butyl DEMP


Liquid Permeation of the EPDM With DIMP
Signal (V)
0.3
0.2
0.1
0
0
10000
20000
30000
40000
50000
Time (s)
T_s
Beginning of Steady State Penetration
$T_{1/2}$
Time at ½ the Steady State Penetration is reached.
T_b
Time at Initial Break

Preliminary Comparison of Equilibrium Sorption into Silicone Elastomer, PDMS: Bis(2-chloroethylsulfide) (Code: HD) vs Chloroethyl Phenyl Sulfide (Code: CEPS) at ca 35 degrees C

Lab	Liquid	Polymer Code	Thickness, mm (mils)	Sorption, Wt/Wt%	Time, hours @ Temperature, degree C
ECBC	HD	PDMS	0.72(28.3)	4.44	1 day
ECBC	HD	PDMS	0.72(28.3)	4.48	4 days
ECBC	CEPS	PDMS	0.72 (28.3)	8.83	1 day
ECBC	CEPS	PDMS	0.72 (28.3)	9.34	6 days
Natick	CEPS	PDMS	3.2 (124.9)	8.2	4 Days

Values are not Final, but for Preliminary Comparison

Accomplishments and Current Status

Accomplishments:

1. Developed Permeation Test Method
2. Successfully Designed Permeation Prototype Cell
3. Manufactured 32 Test Cells to Support Testing
4. Identified 3 Elastomeric Barrier Materials to Test
5. Identified Chemicals for CWA Candidate Simulants
6. Conducted Solubility and Permeation Tests with the Candidate Simulants

Current Status: Conducting Permeation and Solubility Tests with GB and HD to Develop a Correlation

Potential Benefits of Simulant Permeation Study:

1. Provides data so manufacturers can make a determination on potential pretest simulants.

2. Assists manufacturers in their decision of selecting barrier materials based on scientific information; reducing product development times and costs.

3. Expedites availability of new respirators and materials technology for the users.

Summary/Conclusion

- To identify through research chemical compound(s) that can be used as adsorption simulants and to identify pertinent reports that are available to the public.
- Identify simulants and a rapid, relatively low cost laboratory procedure that can be used by manufacturers for estimating CWA permeation through barrier materials.
- Write a draft NIOSH Guidance Document that describes test procedures, simulants and results of agent permeation tests.
- NIOSH or SBCCOM will not guarantee the simulants identified will work on all materials and their correlation coefficient to CWA.
- Passage of manufacturer's pretest with the simulant does not guarantee passage of the official NIOSH certification testing.

Liquid / Vapor Permeation at 35 °C

Sample	Simulant	$T_{b,}$ h	$T_{1/2,}$ h	$T_{s,}$ h	P, v	$\Delta W/W_{0,}$ %	S, %
Silicone							
128 mil	DCH	0.71	3.7	22.2	2.80	7.9	21.6
126 mil	CEPS	1.2	6.1	23.3	0.364	3.2	8.2
128 mil	DEMP	2.6	5.1	15.9	1.23	1.5	7.5
126 mil	DIMP	2.6	6.5	24.5	1.71	4.3	31.8
Butyl							
11 mil	DCH	0.20	0.40	1.93	2.87	4.6	46.6
12 mil	CEPS	0.58	1.0	14.0	0.334	6.7	21.6
14 mil	DEMP	1.3	4.3	10.2	0.137	0.0	0.6
13 mil	DIMP	2.0	3.7	9.0	0.356	0.0	0.5
EPDM							
19 mil	DCH	0.28	0.80	4.1	2.94	4.0	13.4
29 mil	CEPS	1.1	2.7	15.2	0.348	3.4	10.2
18 mil	DEMP	1.1	2.6	10.2	0.141	0.1	
18 mil	DIMP	1.4	3.4	15.2	0.262	0.4	

- T_b is breaktime
- $T_{1/2}$ is time at 50% of steady state permeation
- T_s is time to achieve steady state
- P is the concentration-dependent voltage
- $\Delta W/W_0$ is wt% simulant absorption in test specimen
- S is wt% solubility from immersion experiment